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EXCEPTIONAL HINDRANCE OF INTERNAL ROTATION OF HYDROXYL GROUP IN THE 2,6-Di-t-BUTYL-4-METHYLPHENOL CATION RADICAL STUDIED BY ESR TECHNIQUE

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ESR spectrum of 2,6-di-t-butyl-4-methylphenol cation radical was measured. In this radical, it can be expected that the strong steric repulsion between hydroxyl group and the neighboring t-butyl groups prevents hydroxyl group being coplanar with the aromatic plane. Nevertheless, the experimental results exhibit that the hydroxylic hydrogen is close to the plane of aromatic ring.

Since Bolton and Carrington$^{1)}$ reported the ESR study of duroquinol cation radical, where the existence of rotational isomers was predicted, a number of ESR studies for hydroxyl substituted aromatic cation radicals, such as hydroquinone, 1,4-dihydroxynaphthalene, and 9,10-dihydroxyanthracene cation radicals, have been reported.$^{2-8)}$ Nevertheless, the ESR studies of the cation radicals of phenol or phenol derivatives have not been reported.

In the present communication, we will report the ESR study of 2,6-di-t-butyl-4-methylphenol cation radical (I). As is well known, the 2,6-di-t-butylphenol derivatives are the parent compounds of the phenoxyl neutral radicals and it becomes very interesting to investigate electronic structure of these cation radicals in connection with that of phenoxyl neutral radicals.$^{9)}$

The cation radical I was prepared, in vacuo, by oxidation with $AlCl_3$ in CH_2Cl_2 solvent in an acetone-dry ice bath. The cation radical was stable only at temperature lower than -50°C. The ESR spectrum was recorded at 5°C intervals in the temperature range from -60 to -100°C.

The ESR spectrum of cation I recorded at -80°C is shown in Fig. 1. The hyperfine splittings are observed from three groups 3, 1, and 1 equivalent protons. The largest quartet splitting (14.19 G) was easily assigned to those of methyl protons (a_p^R). The assignment of the other two splittings was not instinctive.

The experimental results obtained for the hydroxylated and methoxylated aromatic cation radicals, such as hydroquinone$^{8f)}$ (1,4-dimethoxybenzene$^{8e)}$), 1,4-dihydroxynaphthalene$^{8f)}$ (1,4-dimethoxynaphthalene$^{8e)}$), and 9,10-dihydroxyanthracene$^{8f)}$ (9,10-dimethoxyanthracene$^{8e)}$), indicated that the hyperfine coupling constants of hydroxylated compounds fairly resemble to those of corresponding methoxylated compounds. As compared with the hyperfine coupling constants of anisole cation radical studied by O'neill et al.,$^{10)}$ the remaining hyperfine splittings were assigned as follows; the larger doublet splitting (3.72 G) was attributed to a

Fig. 1. ESR spectrum of the cation radical of 2,6-di-t-butyl-4-methylphenol observed at -80°C.

hydroxylic proton (a_1^{OH}), and the other doublet (0.89 G) was to one of the two meta protons (a_m^H), but the hyperfine splitting arising from the residual meta proton vanishes to the order of the line-width (~400 mG). The t-butyl proton splitting was not detected in the observed temperature range. Observed hyperfine coupling constants are listed in Table 1. Thus, ESR spectrum of cation I was not explainable unless the nonequivalent values of the meta ring proton splitting were assumed. In the observed temperature range, neither evidence of line-width alternation nor the explicit temperature dependence of hydroxylic proton hyperfine coupling constant was detected.

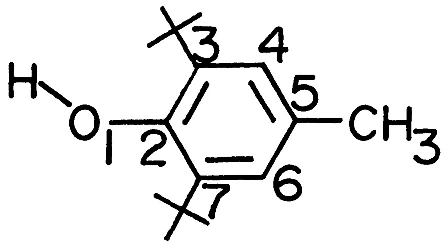
The phenomena of nonequivalent ring meta (or ortho) proton hyperfine splitting were already reported for hydroquinone,8h) duroquinol,8a) and 4,4'-dihydroxybiphenyl 8g) cation radicals, where the hydroxyl group lies in the aromatic plane and two rotational isomers (cis and trans) exist at low temperature. Increasing temperature, the ESR spectra of these radicals exhibit the evidence of line-width alternation.

According to the investigation of hindered internal rotation of hydroxyl group by Sallivan et al.,8) the main factor which is expected to affect the rotational potential function of hydroxyl group is the double bond character of the C-O bond which will tend to constrain the hydroxyl group in the aromatic ring plane. The next factor is steric replusion which will try to force the group out of plane. That is, for the hydroquinone cation radical the potential barrier height of the hydroxyl group is estimated to be ~10 kcal/mol.8a) On the other hand, for the duroquinol cation radical the potential barrier height is lowered by the steric replusion due to methyl group (estimated to be ~4 kal/mol).8a)

In the present radical I, the equilibrium conformation of hydroxyl group is thought to be extremely destabilized by strong steric repulsion due to the neighboring t-butyl group. Therefore, we can expect the less restricted rotation of the hydroxyl group and consequently the large temperature dependence of hydroxylic proton hyperfine splitting.

Table 1. The Observed and Calculated Hyperfine Coupling Constants (G)

Compounds		a_1^{OH}	$a_3^{t\text{-}B}$ (a_3^H)*	$a_7^{t\text{-}B}$ (a_7^H)*	a_4^H	a_6^H	a_5^R (a_5^H)*	Notes
Radical 1	Exptl	3.72	——	——	0.89	<0.40	14.19	(a)
	Calcd	4.65$^{f)}$ 3.72$^{ff)}$	——	——	0.88	0.25	7.91$^{h)}$	
Anisole*	Exptl	4.83	4.51	5.51	1.00	0.21	9.97	ref.10
	Calcd	4.77$^{g)}$	4.52	5.37	1.18	0.48	8.71	(b)



Ring proton splittings calculated assuming $Q_H=|27|G$.

a) $\alpha_o=\alpha+1.93\beta$, $\alpha_3=\alpha-0.10\beta$, $\alpha_5=\alpha-0.16\beta$, $\alpha_7=\alpha-0.14\beta$, $\beta_{o-c}=1.12\beta$.

b) $\alpha_o=\alpha+1.93\beta$, $\alpha_3=\alpha-0.04\beta$, $\beta_{o-c}=1.12\beta$,

f) Calculated from Eq. 1 assuming $\theta=0°C$, $Q_o=-30G$, $Q_c=+40G$.

ff) Calculated from Eq. 1 assuming $\theta=15°C$, $Q_o=-30G$, $Q_c=+40G$.

g) Calculated assuming $Q_{OCH_3}=|30|G$

h) Methyl proton splittings calculated assuming $Q_{CH_3}=|27|G$. The discrepancy between calculated and observed methyl proton splittings will be understood, if the hyperconjugative effect of methyl group is considered.

Surprisingly enough, the experimental results obtained for the cation I exhibit that the hydroxyl group is fairly constrained near the aromatic ring plane.

With the aid of the assumption that the hydroxyl group lies in the aromatic plane, the McLachlan HMO calculation was made using the parameters, $\alpha_o=\alpha+1.93\beta$, $\beta_{c-o}=1.12\beta$ for the OH group, which give good agreement for the 4,4'-dihydroxylbiphenyl cation.8g) The inductive parameters of methyl and t-butyl groups were estimated to be $\alpha_5=\alpha-0.16\beta$ and $\alpha_3=\alpha_7=\alpha-0.14\beta$, respectively. The effect of the planarity of hydroxyl group was taken into account by the addition of an auxiliary parameter 0.04β to the α_3.8g) This calculation gives the results shown in Table 1 and is in agreement with experimental values of the anisole cation.10) For the cation radical I, the calculated hyperfine coupling constants satisfactorily accounted for the observed values of two different meta ring proton splittings, but a discrepancy has been observed between calculated and experimental hyperfine coupling constants of hydroxylic proton.

Recently, it has been pointed out that the temperature dependence of hydroxylic proton hyperfine coupling constant can be understood in terms of a restricted rotation of the hydroxyl group and the hydroxylic proton hyperfine splitting can be expressed by the following equation.8f)

$$a^{OH} = \langle\cos^2\theta\rangle Q_o\rho_o^\pi + \langle\sin^2\theta\rangle Q_c\rho_c^\pi \qquad (1)$$

where ρ_o^π and ρ_c^π are the spin densities on the oxygen atom (ρ_o^π) and on the carbon atom (ρ_c^π) bonded to the OH group, respectively, and θ is the angle between the C-OH plane and the nodal plane of the π system. The values of Q_o and Q_c are experimentally determined to be -35±5 G and 50±10 G, respectively.

Using Eq. 1, the calculated hyperfine coupling constant of hydroxylic proton coincides with the experimental value, if the averaged value of the angle, θ, is estimated to be 15° based on the calculated spin densities.

Recently Itoh et al.,11) determined the molecular geometry of 3,5-di-t-butyl-4-hydroxybenzylidenemalononitrile at room temperature. According to the results of the X-ray analysis for the above compound, the hydroxyl group lies in the aromatic ring plane and is sandwiched by two methyl groups in the t-butyl group.

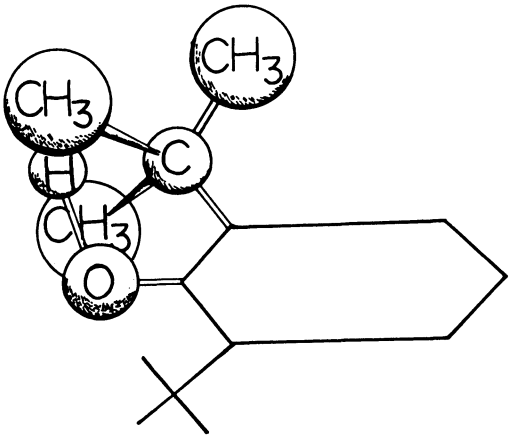


Fig. 2. Geometrical structure assumed for cation radical of 2,6-di-t-butyl-4-methylphenol.

A similar situation probably exists in the present case. It can be considered that the hydroxyl group in radical I is also sandwiched by two methyl groups of the t-butyl group (see Fig. 2) and is rapidly oscillating around the equilibrium conformation, affected by the vibration of t-butyl group.

This conformation is more or less qualitative. It, however, sufficiently explains the experimental results that the ESR spectrum of cation I exhibits neither the evidence of line-width alternation nor the temperature dependence of hydroxylic proton splitting.

Preparation of the 4-alkylphenol cation radicals, such as 4-methyl and 4-ethylphenol, was tried but we failed to detect the ESR absorptions of these radicals. This implies that the presence of the t-butyl groups stabilizes the hindered phenol cation radical.

References and Notes

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